



Short communication

A platinum film with organized pores for the counter electrode in dye-sensitized solar cells



Chun-Chieh Wang^a, Jian-Ging Chen^a, Kuan-Chieh Huang^a, Hsin-Wei Chen^a, Ying-Chiao Wang^b, Chih-Yu Hsu^a, R. Vittal^a, Jiang-Jen Lin^b, Kuo-Chuan Ho^{a,b,*}

^aDepartment of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^bInstitute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

HIGHLIGHTS

- A Pt film with nano-pores could be electro-deposited using a PS template.
- The DSSC with a templated Pt film shows a high power-conversion efficiency.
- The high efficiency is attributed to the high surface area of the templated Pt.
- An efficiency of 8.89% is achieved for the DSSC under 1 sun condition.

ARTICLE INFO

Article history:

Received 12 May 2012

Received in revised form

24 March 2013

Accepted 31 March 2013

Available online 8 April 2013

Keywords:

Counter electrode

Dye-sensitized solar cell

Platinum

Polystyrene template

ABSTRACT

A platinum (Pt) film is electro-deposited into the voids of a polystyrene (PS) template on an FTO glass. After the removal of the template by heating, the Pt film forms a novel submicron structure with organized pores in it (designated as e-PtOP). The FTO glass with this Pt structure is used as the counter electrode (CE) for a dye-sensitized solar cell (DSSC). Higher surface area, and thereby higher electrocatalytic ability of the e-PtOP render higher short-circuit current density for the pertinent DSSC (18.94 mA cm^{-2}) than that of the cell with a Pt film obtained without PS template (16.63 mA cm^{-2}). A thin layer of Pt is further sputtered onto the e-PtOP to render an increased fill factor of the DSSC with the corresponding CE. Consequently, the power-conversion efficiency of this cell is thus enhanced from 6.03 to 8.89%, with reference to the cell with a Pt film obtained without PS template.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The dye-sensitized solar cell (DSSC) consists of a dye-adsorbed nanocrystalline TiO_2 photoanode, an electrolyte, and a counter electrode (CE). Conventionally, a platinum (Pt) layer is coated on a conductive substrate of the CE not only for obtaining a superior catalytic surface on the substrate, but also for minimizing the voltage loss due to charge transfer overpotential at the CE [1,2]. The Pt-coated CE of DSSCs could be of two types: one from a composite of Pt and other material, such as NiP [3], acetylene-black (AB) [4], SnO_2 [5], carbon black [6], polypyrrole [7], and multi-wall carbon nanotube (MWCNT) [8], and the other from Pt nano-clusters [9–14], composed of only Pt nanoparticles.

It is anticipated that a Pt composite combines the advantages of both Pt and its composite material. Low Pt-loaded Pt:SnO_2 paste, mixed with ethylcellulose/terpineol, was coated on a transparent conducting oxide glass to reduce Pt agglomeration and thereby to increase catalytic surface area of the film [5]. An improved electrocatalytic ability of CE based on a thin film consisting of Pt nanoparticles and MWCNTs was observed due to its large surface area [8]. In addition, pulse current [9] and initial pulse potential [10] electrodeposition techniques were used to obtain Pt nanoparticles and round textured Pt clusters, respectively; the films of these particles and clusters showed high surface areas, and enabled high performances to DSSCs.

In this work, we have prepared an electro-deposited Pt film with organized pores (hereafter designated as e-PtOP) on the FTO glass, by using polystyrene (PS) template. The morphology of this film was intrinsically unique and never reported before. The DSSC with the e-PtOP showed a higher photocurrent density and power-conversion efficiency (η) than the cell with the Pt film electro-deposited without

* Corresponding author. Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan. Tel.: +886 2 2366 0739; fax: +886 2 2362 3040.

E-mail address: kcho@ntu.edu.tw (K.-C. Ho).

the PS template (hereafter designated as e-Pt). Moreover, the e-PtOP was further treated by sputtering Pt on it. After this sputtering treatment, the pertinent DSSC showed an excellent η of 8.89%.

2. Experimental

The FTO glass (sheet resistivity = $10 \Omega \text{ sq}^{-1}$, NSG America, Inc.) was vertically placed in a container containing a colloidal suspension with 0.05 wt% monodispersed particles of carboxyl-PS (average size = 300 nm, Invitrogen Life Technologies). The container was placed in an oven at 55 °C; with the evaporation of the solvent, and due to capillary forces, the carboxyl-PS spheres had compactly self-assembled on the FTO glass. The FTO glass with the solvent-evaporated PS template was then cleaned with ethanol and annealed at 80 °C for 2 h to promote necking of the PS spheres, which is necessary for the structural stability of the template [15].

Pt films were deposited on FTO glasses, with and without the PS template, by cyclic voltammetry (CV) method, using a three-electrode system (CH Instruments) [16], and the obtained electrodes were used as the CEs of DSSCs. The FTO glass with solvent-evaporated PS template, a Pt wire, and an Ag/Ag⁺-electrode were

used as the working, counter, and reference electrode, respectively. The working electrode was immersed into an ethanol solution containing 10 mM dihydrogen hexachloroplatinate (H_2PtCl_6). Pt nanoparticles could be deposited in the voids of the PS template by cycling the potential from -1.0 to 1.0 V (vs. Ag/Ag⁺) [16], at a scan rate of 50 mV s⁻¹. The Pt-deposition was stopped at an applied charge density of 1.0 C cm^{-2} . After the electrodeposition, the FTO glass with Pt-filled PS template was annealed at 385 °C for 15 min to remove the carboxyl-PS [1]. In comparison, an e-Pt film was electro-deposited, under the same conditions, however without using the PS template.

The N719 dye-absorbed TiO₂ photoanode was prepared according to the literature [8], and coupled with the CE (e-PtOP or e-Pt) within a distance controlled by a 25 μm-thick spacer (Surlyn®, Solaronix). The electrolyte containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine in ACN/3-methoxypropionitrile (v/v = 1:1), was injected into the space between the two electrodes by capillary force. Photocurrent density–voltage (J – V) curves of the DSSCs were obtained by employing a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands). The DSSC was illuminated

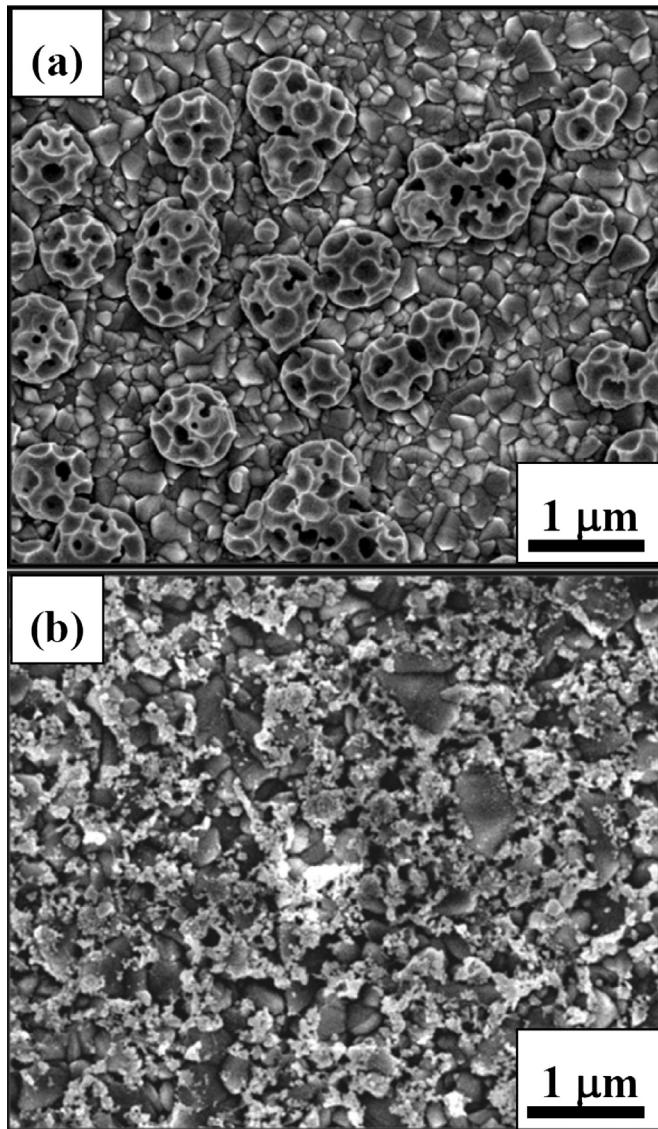


Fig. 1. SEM images of (a) e-PtOP and (b) e-Pt.

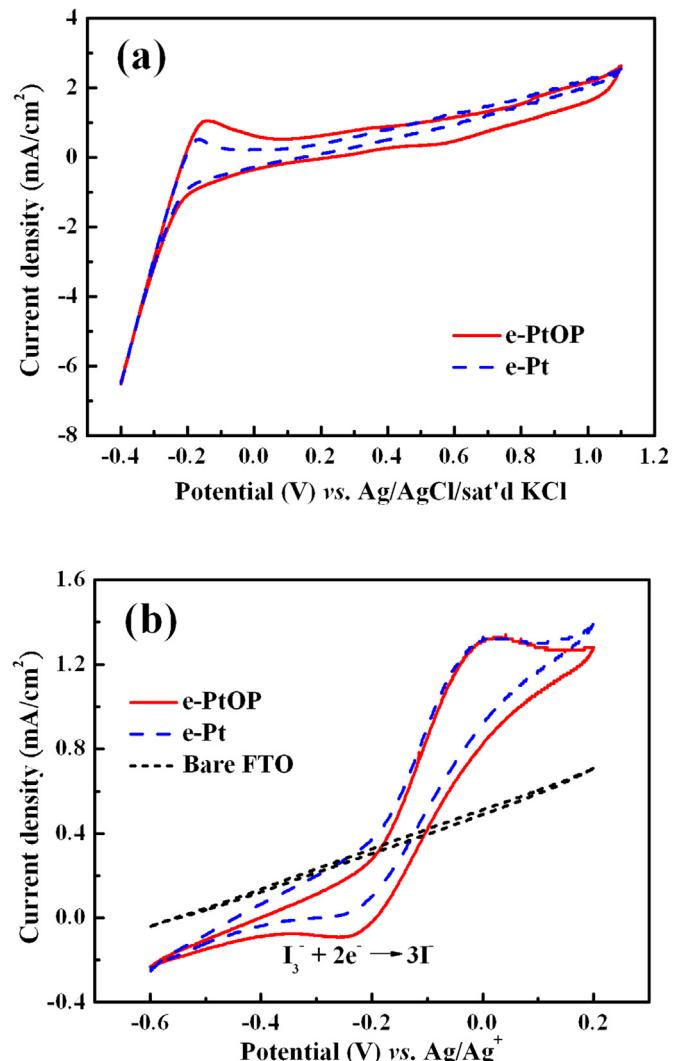


Fig. 2. (a) CVs of the e-PtOP and e-Pt obtained in 0.5 M H_2SO_4 at a scan rate of 50.0 mV s^{-1} and at fixed charge density of 1.0 C cm^{-2} . (b) CVs of the e-PtOP and e-Pt, in ACN solution containing 10.0 mM LiI, 1.0 mM I₂, and 0.1 M LiClO₄.

by a class A quality solar simulator (PEC-L11, AM 1.5G, Peccell Technologies, Inc.).

3. Results and discussion

The surface morphology of the e-PtOP, obtained by electrodeposition on an FTO glass using a PS template, is shown in Fig. 1a. It is generally accepted that H_2PtCl_6 reduces to form Pt nanoparticle in the voids of the PS template [16]. Metallic Pt could deposit randomly from the bottom to the top of the voids, and the corresponding structured Pt was obtained after PS was removed. On the other hand, the surface morphology of e-Pt does not exhibit any defined structure (Fig. 1b). This finding suggests that the surface area of the e-PtOP is larger than that of the e-Pt. We estimated the surface areas of these two films by CV, performed in a 0.5 M H_2SO_4 solution at a scan rate of 50 mV s⁻¹ (Fig. 2a). The real surface areas (A_r) of the films of e-PtOP and e-Pt were estimated by integrating the charges under the anodic peaks of their CVs ranging from -0.3 to 0.2 V (vs. Ag/AgCl/sat'd KCl), followed by subtracting the charge associated with the double layer in the corresponding range of potentials [17]. In addition, a conversion factor of 208 $\mu\text{C cm}^{-2}$ was used for the calculation. The geometric surface areas (A_g) of the films were controlled to be 1.0 cm^2 . Thus, a relatively larger surface roughness (A_r/A_g) of 14.93 of the e-PtOP is obtained in comparison to that of the e-Pt ($A_r/A_g = 8.73$).

The electro-catalytic abilities of e-Pt and e-PtOP were studied by CV. In brief, the CVs were obtained in an ACN-based solution containing 10.0 mM LiI , 1.0 mM I_2 , and 0.1 M LiClO_4 , using a Pt foil as the CE and an Ag/Ag⁺ reference electrode, at a scan rate of 50 mV s⁻¹. In Fig. 2b, the value of the cathodic peak current density corresponding to $\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$ for the e-PtOP is higher than that of the

Table 1

(a) Photovoltaic parameters of the DSSCs with the e-Pt, e-PtOP, and e-PtOP with post-treatment, obtained at a light intensity of 100 mW cm⁻².

| Counter electrodes | V_{OC} (V) | J_{SC} (mA cm ⁻²) | η (%) | FF |
|----------------------------|---------------------|--|------------|------|
| e-Pt | 0.76 | 16.63 | 5.79 | 0.46 |
| e-PtOP | 0.71 | 18.94 | 6.03 | 0.45 |
| e-PtOP with post-treatment | 0.76 | 18.88 | 8.89 | 0.62 |

e-Pt, i.e., the electro-catalytic ability of the e-PtOP is better than that of the e-Pt; thus a higher performance is expected for the DSSC employing a CE with the e-PtOP than that of the cell with the e-Pt [8].

Fig. 3a shows J – V curves of the DSSCs with the e-PtOP CE and the e-Pt CE under 1 sun condition. The corresponding open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and η are listed in Table 1. The higher J_{SC} of the DSSC with the e-PtOP CE is apparently due to the larger surface area of the e-PtOP available for the reduction of I_3^- ions. However, the V_{OC} of the cell with the e-PtOP CE is less than that of the cell with the e-Pt CE. The submicron structure of the e-PtOP is apparently the reason for causing this. Namely, the e-PtOP film with a submicron thickness would encounter a larger potential difference from its bottom points to its peak points due to the internal resistance of the e-PtOP film (Fig. 3b). In fact, a Pt film having a thickness of 2.0 nm is sufficient for the reduction of I_3^- ions [18]. We attribute this high electro-catalytic ability of the CE with the e-PtOP to the pores itself, where the bottom points are close to the substrate and have high surface area.

To ameliorate the Pt-coverage of the FTO glass, a post-treatment, performed using sputtering Pt (20 mA, 30 s) on the e-PtOP, was used. Fig. 3a shows the J – V curves of the DSSCs with a CE based on e-PtOP with post-treatment, and the corresponding photovoltaic parameters are summarized in Table 1. The V_{OC} and FF of this DSSC have both increased tremendously with the post-treatment of the film; however, its J_{SC} remained to be the same. Sputtering Pt film has apparently covered the above-mentioned bottom points in the e-PtOP, and has facilitated the I_3^- reduction. This favorable reduction of I_3^- ions at the Pt-sputtered film could render a higher V_{OC} to its cell, because of non-availability of I_3^- for the recombination reactions. Additional Pt-sputtered layer at the bottom points of the e-PtOP is also favorable for high conductivity of the film, and this is reflected by the greatly increased FF in favor of the cell with the corresponding CE. Consequently, the DSSC with the e-PtOP using post-treatment has shown an outstanding η of 8.89%.

4. Conclusions

A film of e-PtOP could be electro-deposited using a PS template. The surface morphology of the film was unique in its nature, which has never been reported before. The e-PtOP showed a higher electro-catalytic ability than that of the e-Pt. The DSSC with the e-PtOP CE showed a higher J_{SC} and η than those of the cell with the e-Pt CE; this is attributed to the higher surface area of the e-PtOP. Furthermore, an excellent η of 8.89% was achieved for the cell with an e-PtOP CE sputtered with a thin layer of Pt (post-treatment). The significant improvement in the performance of the DSSC with the e-PtOP CE with the post-treatment is attributed both to the morphology of the film and its subsequent treatment with sputtering Pt.

Acknowledgments

This work was financially supported by the National Science Council (NSC) of Taiwan.

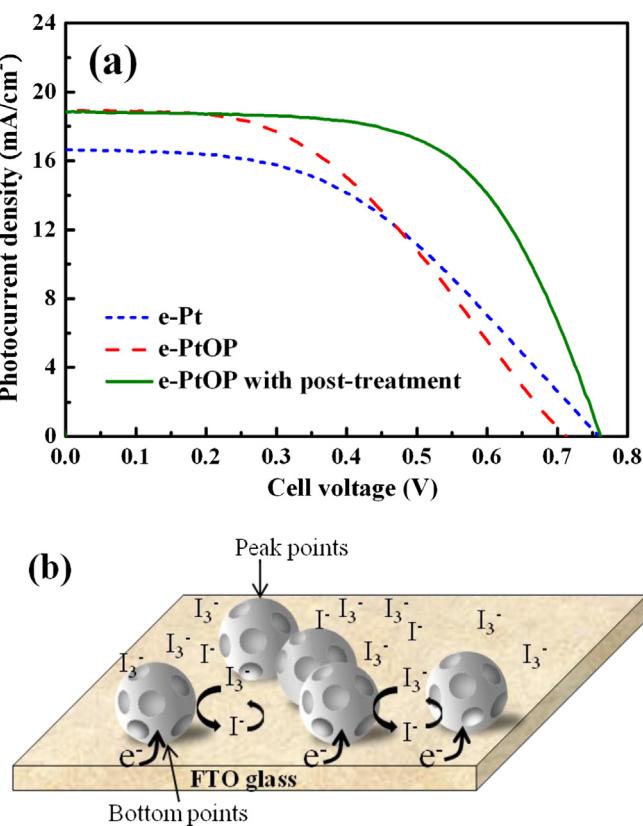


Fig. 3. (a) J – V curves of the DSSCs with the e-Pt, e-PtOP, and e-PtOP with post-treatment (1 sun). (b) The illustration of the e-PtOP with peaks and bottom points owing to its porous nature.

References

- [1] N. Papageorgiou, *Coord. Chem. Rev.* 248 (2004) 1421–1446.
- [2] T. Hoshikawa, M. Yamada, R. Kikuchi, K. Eguchi, *J. Electroanal. Chem.* 577 (2005) 339–348.
- [3] G. Wang, R. Lin, Y. Lin, X. Li, X. Zhou, X. Xiao, *Electrochim. Acta* 50 (2005) 5546–5552.
- [4] F. Cai, J. Liang, Z. Tao, J. Chen, R. Xu, *J. Power Sources* 177 (2008) 631–636.
- [5] G. Khelashvili, S. Behrens, A. Hinsch, W. Habicht, D. Schild, A. Eichhofer, R. Sastrawan, K. Skupien, E. Dinjus, H. Bönnemann, *Thin Solid Films* 515 (2007) 4074–4079.
- [6] P. Li, J. Wu, J. Lin, M. Huang, Y. Huang, Q. Li, *Solar Energy* 83 (2009) 845–849.
- [7] S.S. Jeon, C. Kim, J. Ko, S.S. Im, *J. Phys. Chem. C* 115 (2011) 22035–22039.
- [8] K.C. Huang, Y.C. Wang, R.X. Dong, W.C. Tsai, K.W. Tsai, C.C. Wang, Y.H. Chen, R. Vittal, J.J. Lin, K.C. Ho, *J. Mater. Chem.* 20 (2010) 4067–4073.
- [9] S.S. Kim, Y.C. Nah, Y.Y. Noh, J. Jo, D.Y. Kim, *Electrochim. Acta* 51 (2006) 3814–3819.
- [10] G. Tsekouras, A.J. Mozer, G.G. Wallace, *J. Electrochem. Soc.* 155 (2008) K124.
- [11] N. Papageorgiou, W.F. Maier, M. Gratzel, *J. Electrochem. Soc.* 144 (1997) 876–884.
- [12] T.C. Wei, C.C. Wan, Y.Y. Wang, *Appl. Phys. Lett.* 88 (2006) 103122.
- [13] T.C. Wei, C.C. Wan, Y.Y. Wang, C.M. Chen, H.S. Shiu, *J. Phys. Chem. C* 111 (2007) 4847–4853.
- [14] J.L. Lan, Y.Y. Wang, C.C. Wan, T.C. Wei, H.P. Feng, C. Peng, H.P. Cheng, Y.H. Chang, W.C. Hsu, *Curr. Appl. Phys.* 10 (2010) S168–S171.
- [15] E.S. Kwak, W. Lee, N.G. Park, J. Kim, H. Lee, *Adv. Funct. Mater.* 19 (2009) 1093–1099.
- [16] Y. Liu, J. Chen, V. Misoska, G.F. Swiegers, G.G. Wallace, *Mater. Lett.* 61 (2007) 2887–2890.
- [17] A. Zolfaghari, G. Jerkiewicz, *J. Electroanal. Chem.* 420 (1997) 11–15.
- [18] X. Fang, T. Ma, G. Guan, M. Akiyama, T. Kida, E. Abe, *J. Electroanal. Chem.* 570 (2004) 257–263.